Xenon $N_{4,5}OO$ spectrum – a useful calibration source

T. X. Carroll[a], J. D. Bozek[b], E. Kukk[c], V. Myrseth[d], L. J. Sæthre[d], T. D. Thomas[e,*], and Karoline Wiesner[f]

[a] *Keuka College, Keuka Park, NY 14478, USA*
[b] *Advanced Light Source, Lawrence Berkeley National Laboratory, University of California, Berkeley, CA 94720 , USA*
[c] *Department of Physics, University of Oulu, FIN-90570, Finland*
[d] *Department of Chemistry, University of Bergen, N-5007 Bergen, Norway*
[e] *Department of Chemistry, Oregon State University, Corvallis, OR 97331-4003, USA*
[f] *Department of Physics, Uppsala University, S-75121 Uppsala, Sweden*

Abstract
In the xenon $N_{4,5}OO$ Auger spectrum there are 19 prominent lines ranging from 8 to 36 eV that provide a convenient set of standards for calibrating electron spectrometers. Combining optical data with recent measurements of this spectrum gives energies for these lines that are absolutely accurate to 11 meV. For most lines the relative accuracy is better than 1 meV; for a few it is about 3 meV. The spin-orbit splitting of the xenon 4d lines is measured to be 1979.0±0.5 meV.

Keywords: Auger, photoelectron, spin-orbit, calibration, xenon 4d
*Corresponding author. Tel. +1-541-737-6711; fax: +1-541-737-2062
E-mail address: thomast@chem.orst.edu

D:\My Documents\Manuscripts\Xenon\Xe Auger as a calibration.wpd
3:03 pm 6 February 2002

1. Introduction

Electron kinetic-energy spectra are typically obtained by measuring counting rate of the electrons detected in the spectrometer as a function of a voltage applied to the spectrometer. Ideally the kinetic energy is linearly related to this voltage with unit slope. In the real world, however, it is possible (and even likely) that the slope is not exactly one, that the scale is not exactly linear, and that there is an offset between the true and apparent kinetic energy scales. In typical systems the offset can be greater than 1 eV. Thus, calibration of the spectrometer requires a knowledge of the absolute voltage, the slope, and the linearity of the scan. For this purpose, it is useful to have convenient standards spanning a range of kinetic energies by which these quantities can be measured.

A useful standard for this purpose is the xenon $N_{4,5}OO$ Auger spectrum, which has 19 prominent lines ranging in kinetic energy from 8 to 36 eV. This spectrum is excited with good intensity with photons whose energy is above the $4d_{3/2}$ threshold (69.5 eV). The relative energies of some of these lines are known with high accuracy from optical measurements. The absolute energies can be determined by combining the optical energies with the 4d ionization energies. With this information, the energy scale can be calibrated and the peak energies for which optical data are not available can be measured.

Results of such measurements have been given by Werme et al.[1], Aksela et al.[2], and Southworth et al. [3] In each case, however, there is room for improvement in the results presented. For the first two, the calibration was based on only two points in the optical scale and the results are quoted only to the nearest 0.01 eV. In the analysis made by Werme et al., it is not apparent that curve fitting was used to determine the peak positions. For the work of Aksela et al. an extensive fitting procedure was used, but the resolution was not so good as was obtained by Werme et al. or by others more recently [4]. The results given by Southworth at al. have a large uncertainty – 0.05 eV.

It is useful, therefore, to reexamine this question. We present here the results of measurements of this spectrum and of the calibration of the spectrum using optical data. As a result of this analysis, we are able to produce a set of 22 Auger energies with an absolute accuracy of about 11 meV and with a relative accuracy in most cases of better than 1 meV.

2. Experimental procedures

Xenon $N_{4,5}OO$ spectra were measured in three separate experiments, two at the Advanced Light Source (ALS) using beamline 10.0.1 and one at the MAX II synchrotron using beamline I411. In one experiment at the ALS (referred to as ALS1) spectra were measured at 8 photon energies from 93 to 108 eV. In these the electron kinetic energy spectrum covered the range from 18 to 42 eV, and included the 4d photoelectron peaks. In the other two experiments the electron kinetic energy spectrum ranged from about 4 to 40 eV. In one of these (ALS2) the photon energy was 96 eV, and the spectrum includes the 4d photoelectron peaks. In the other (MAX II), the photon energy was 110 eV, and the photoelectron peaks were beyond the scan range. In each case, measurements were made using Scienta SES-200 analyzers, with slits and pass energies chosen to give a resolution of 35 to 40 meV. The three experiments were well separated in time and involved three different voltage

supplies for the analyzers.

The spectra have been fit by least squares to Voigt functions, with intensity, position, Gaussian width, and Lorentzian width as free parameters. All of the Auger peaks were constrained to have the same Gaussian and Lorentzian widths. A linear, sloping background was assumed. Several fits were made, some to an entire spectrum (using as many as 72 peaks) and some to selected portions of the spectrum. For one of the spectra, in which the photoelectron kinetic energies are less than some of the Auger energies, the effects of post-collision interaction were included using eq. 12 from van der Straten et al. [5] The results obtained including post-collision ineraction are essentially the same as those obtained with Voigt-function fits.

3. Calibration

The calibration of the Auger spectrum is based on the use of the first and second ionization energies of xenon (I_1 and I_2) and the energies, E_{ex}, of the various states of Xe^{2+}. The energy of a state in Xe^{2+} (relative to the ground state of xenon) is given by the relationship

$$E(Xe^{2+}) = I_1 + I_2 + E_{ex} \qquad (1)$$

These are combined with the xenon $4d_{5/2}$ ionization energy, $I(4d_{5/2})$, to give the energies of the N_5OO Auger lines through the relationship

$$K = I(4d_{5/2}) - E(Xe^{2+}) \qquad (2)$$

The energies for the N_4OO Auger lines can be obtained either in a similar way from the reported value of the $4d_{3/2}$ ionization energy or from the Auger spectrum using the spin-orbit splitting as one of the fitting parameters. Here we have used the second alternative. The various energies, which have been taken from published literature [6][7][8][9][10] are summarized in Table 1.

The line positions, V, obtained from the least-squares fitting have been fit to the relationship

$$V = V_0 + (K + n \times SO)V_1 \qquad (3)$$

where n = 0 for N_5OO lines and 1 for N_4OO lines, and V_0 and V_1 are fitting parameters. SO is the spin-orbit splitting and is also a fitting parameter. Some fits were made using an additional, quadratic, term, but these showed that such a term is not statistically significant. Once the least-squares values of the parameters have been obtained, the process can be reversed to give experimental values of the kinetic energies. These can be compared with the original values of K to assess the quality of the procedure, or, where no optical values of K are available, they provide new estimates of these quantities.

4. Results

The spectrum measured at MAX II is shown in Fig. 1. The peaks have been numbered using the numbering scheme given by Werme et al. [1] Because the photon energy was 110 eV, the 4d

photoelectron peaks are to be found at energies only slightly higher than shown here and the photoelectron shakeup peaks are found approximately in the middle of the Auger spectrum. The strongest of these are in a region where there are only weak Auger lines, but weaker shakeup peaks are found throughout the low-energy portion of the spectrum. As will be seen below, these can complicate the fitting of the peaks.

4. 1 Spin-orbit splitting

A number of values for the spin-orbit splitting of the xenon 4d level have been reported.[7][8][11][12][13] These are summarized in Table 2, together with the values we have derived from our data using the procedure outlined above. Also included in this table are two values we have derived from the data of Werme et al. [1] and Aksela et al. [2] using the same procedure, as well as a value we have obtained from fitting the xenon 4d photoelectron peaks from eight spectra taken at different photon energies. For our results and for those derived from the data of Werme et al. and Aksela et al. the quoted uncertainties are those obtained from the statistics of the fitting procedures. The weighted average of these measurements gives a spin-orbit splitting of 1979.0±0.5 meV.

4.2 Auger energies

Energies for 22 xenon $N_{4,5}OO$ Auger lines are listed in Table 3. There are three categories of energies: N_5OO energies derived directly from the data of Table 1, N_4OO energies derived from the data in Table 1 plus the value of the spin-orbit splitting mentioned above, and $N_{4,5}OO$ energies that we have derived from our measurements. As in Fig. 1, the energies are numbered according to the numbering scheme given by Werme et al. The absolute uncertainty in all of these numbers is determined primarily by the uncertainty in the $4d_{5/2}$ ionization energy, 10 meV [8], giving an overall absolute uncertainty of 11 meV. Any changes in this ionization energy or its uncertainty will cause corresponding changes in these numbers. The relative uncertainties are much less than this, being less than 1 meV for the first two categories of energies and about 3 meV for the energies determined from our measurements.

A comparison of our measured Auger energies and those based on the data in Table 1 (plus the spin-orbit splitting, where appropriate) is illustrated in Fig. 2. Here we have plotted the difference between the measured and the reference Auger energies versus the kinetic energy. We see that, for the most part, the two sets of data agree within a few meV. There are, however, two places, peaks 15 and 16, where there are much larger discrepancies, and it is useful to consider the source of these. They illustrate the difficulty of obtaining accurate information on line position in the case of a weak peak or of even a prominent peak if it is surrounded by a number of small peaks. The spectra in the regions of these peaks are plotted in Fig. 3 for both the MAX II data and the ALS data. These differ in that the ALS spectrum was measured at a photon energy of 96 eV and shakeup peaks do not contribute in this region of the spectrum. The MAX II spectrum was measured at a photon energy of 110 eV, and, as can be seen in Fig. 1, shakeup makes a significant contribution in this region. Our experience with fitting this portion of the spectrum indicates that the derived peak positions are

sensitive to inclusion of all of the small peaks. Because peak 15 is so weak, we have not used it in our calibration procedure.

Including the data for peak 16, the root-mean-square (rms) deviation of the energies we have measured from those derived from the data in Table 1 is 4 meV for the MAX II data and 2 meV for the ALS data. From these and from other results we have obtained in fitting the data, we conclude that this fitting procedure makes it possible to determine the peak positions with a precision of about 3 meV, as indicated above. Comparable analyses of the data given by Werme et al. and by Aksela et al. give rms deviations of 8 and 13 meV respectively.

5. Discussion

Emerging from these results is some insight into the quality of the analyzers used in this work. From the fits and from inspection of Fig. 2, we can conclude that there is no significant nonlinearity in the voltage supplies. As for the slope, the values of V_1 in eq. (4), which reflects the relationship between the nominal voltage increments and the true voltage increments, are 1.00017(6) for the ALS data and 1.00072(12) for the MAX II data, indicating an accuracy of a few parts in 10^4 in the nominal voltages.

As can be seen from Fig. 1, our choice of a photon energy for the MAX II experiment, 110 eV, leads to significant shakeup structure in the region between 25 and 30 eV as well as to smaller peaks at lower energies. A better choice would be a photon energy greater than 130 eV, which would shift the major shakeup contributions out of the range of the Auger kinetic energies.

The relatively weak peaks 26 and 28 present a problem. These appear to be a spin-orbit doublet, but the spacing between them is only 1962 meV, which is 17 meV lower than the average spin-orbit splitting that we have observed. A similar effect is seen in the results reported by Werme et al. and Aksela et al. In view of the problems mentioned above in fitting weak peaks in the neighborhood of either strong peaks or a large number of even weaker peaks, it seems likely that this discrepancy is merely an artifact of the fitting process.

The energies given in Table 3 should provide a convenient set of calibration points for electron spectrometers at a level of accuracy that is higher than what has been available heretofore.

Acknowledgments

TXC and TDT acknowledge support by the National Science Foundation under Grant No. CHE-9727471. EK and JDB acknowledge support from the Divisions of Chemical and Material Sciences, Office of Energy Research, of the U. S. Department of Energy. LJS and VM thank the Research Council of Norway (NFR) for support.

References

[1] L. O. Werme, T. Bergmark, and K. Siegbahn, Physica Scripta 6 (1972) 141.

[2] H. Aksela, S. Aksela, and H. Pulkkinen, Phys. Rev. A 30 (1984) 865.

[3] S. Southworth, U. Becker, C. M. Truesdale, P. H. Kobrin, D. W. Lindle, S. Owaki, and D. A. Shirley, Phys. Rev. A 28 (1983) 261.

[4] J. Jauhiainen, A. Ausmess, A Kivimäki, S. J. Osborne, A. Naves de Brito, S. Aksela, S. Svensson, and H. Aksela, J. Electron Spectrosc. Relat. Phenom.9 (1994) 181.

[5] P. van der Straten, R. Morgenstern, and A. NIehaus, Z. Phys. D 8 (1988) 33.

[6] C. E. Moore, Atomic Energy Levels, Vol. III, NSRDS-NBS 35 (U. S. Governement Printing Office, Washington, D. C., 1971).

[7] J. E. Hansen and W. Persson, Physica Scripta 25 (1982) 487.

[8] K. Codling and R. P. Madden, Phys. Rev. Lett. 12 (1964) 106.

[9] G. C. King, M. Tronc, F. H. Read, and R. C. Bradford, J. Phys. B: Atom. Molec. Phys. 10 (1977) 2479

[10] J. E. Hansen, F. G. Meijer, M. Outred, W. Persson, and H. O. Di Rocco, Physica Scripta 27 (1983) 254.

[11] U. Gelius, J. Electron Spectrosc. Relat. Phenom. 5 (1974) 985.

[12] B. W. Yates, K. H. Tan, L. L. Coatsworth, and G. M. Bancroft, Phys. Rev. A 31 (1985) 1529.

[13] A. Ausmees, S. J. Osborne, R. Moberg, S. Svensson, S. Aksela, O.-P. Sairanen, A. Kivimäki, A. Naves de Brito, E. Nõmmiste, J. Jauhiainen, and H. Aksela., Phys. Rev. A 51 (1995) 855.

Table 1. Energies used in calculating the xenon N_5OO Auger energies. Uncertainties in the last digit are given in parentheses.

	cm^{-1}	eV[a]	Ref
I_1	97834.4	12.1299	5
I_2	169175(30)	20.975(4)	6
I ($4d_{5/2}$)		67.548(11)	7,8
$5s^25p^4\ ^3P_2$	0	0	
$5s^25p^4\ ^3P_1$	9794.6	1.2144	6
$5s^25p^4\ ^3P_0$	8130.7	1.0081	6
$5s^25p^4\ ^1D_2$	17099.0	2.1200	6
$5s^25p^4\ ^1S_0$	36102.9	4.4762	6
$5s5p^5\ ^3P_2$	98263	12.1831	5
$5s5p^5\ ^3P_1$	103569	12.8409	5
$5s5p^5\ ^1P_1$	119026.28	14.7574	5
$5s^25p^35d^1$ (J=1)[b]	154639.61	19.1729	5
$5s^05p^6\ ^1S_0$	210857.55	26.1430	9

a. Values in cm^{-1} have been converted to electron volts by dividing by 8065.544.
b. In ref. 5 this state is designated $5s^25p^36s$. The notation here is that given in ref. 2.

Table 2. Xenon 4d spin-orbit splitting. Uncertainties in the last decimal place are given in parentheses.

Method	Value (meV)	Reference
Photon absorption	1977(10)	7
Auger	1985(4)	a
XPS	1980(10)	10
Electron Energy Loss	1989(3)	8
Auger	1971(7)	b
XPS	1979(7)	11
XPS	1982(2)	12
XPS	1977(1)	This work, ALS1[c]
Auger	1978(1)	This work, ALS1[c]
Auger	1980(2)	This work, ALS2
Auger	1978(2)	This work, MAX II
Weighted average	1979.0(5)	

a. The data of ref. 1 have been analyzed by us to give this value.
b. The data of ref. 2 have been analyzed by us to give this value.
c. Average of 8 measurements

Table 3. Xenon $N_{4,5}OO$ Auger kinetic energies (eV).

Number[a]	Energy	Method	Number[a]	Energy	Method
1	36.422	b	15	22.260	c
2	35.208	b	16	21.665	b
3	34.443	c	18	19.686	c
4	34.302	b	22	17.249	b
5	33.435	c	24	16.146(3)	d
6	33.229	c	25	15.270	c
7	32.323	c	26	14.703(3)	d
8	31.946	b	27	14.169(3)	d
9	29.967	c	28	12.741(3)	d
13	24.239	b	29	10.279	b
14	23.581	b	30	8.300	c

The absolute uncertainty is 11 eV. The relative uncertainties are 1 meV or less, except where indicated by a value in parentheses, which is the uncertainty in the last decimal place.

a. The numbering system is that used by Werme et al. (ref 1).
b. From data given in Table 1 plus the experimentally determined value of the spin-orbit splitting, 1979 meV.
c. From data given in Table 1
d. Determined from measured Auger spectrum

Figure captions

Fig 1. The xenon $N_{4,5}OO$ Auger spectrum measured at a photon energy of 110 eV.

Fig.2. Difference between the kinetic energies derived from the Auger spectra and those derived from optical data. The open circles (ALS) were measured at a photon energy of 97 eV and the closed circles (MAX II) were measured at 110 eV.

Fig. 3. Expanded view of the xenon $N_{4,5}OO$ Auger spectrum for two different experiments in the kinetic energy region 20 to 23 eV. Additional contributions to the MAX II data from shakeup are apparent.

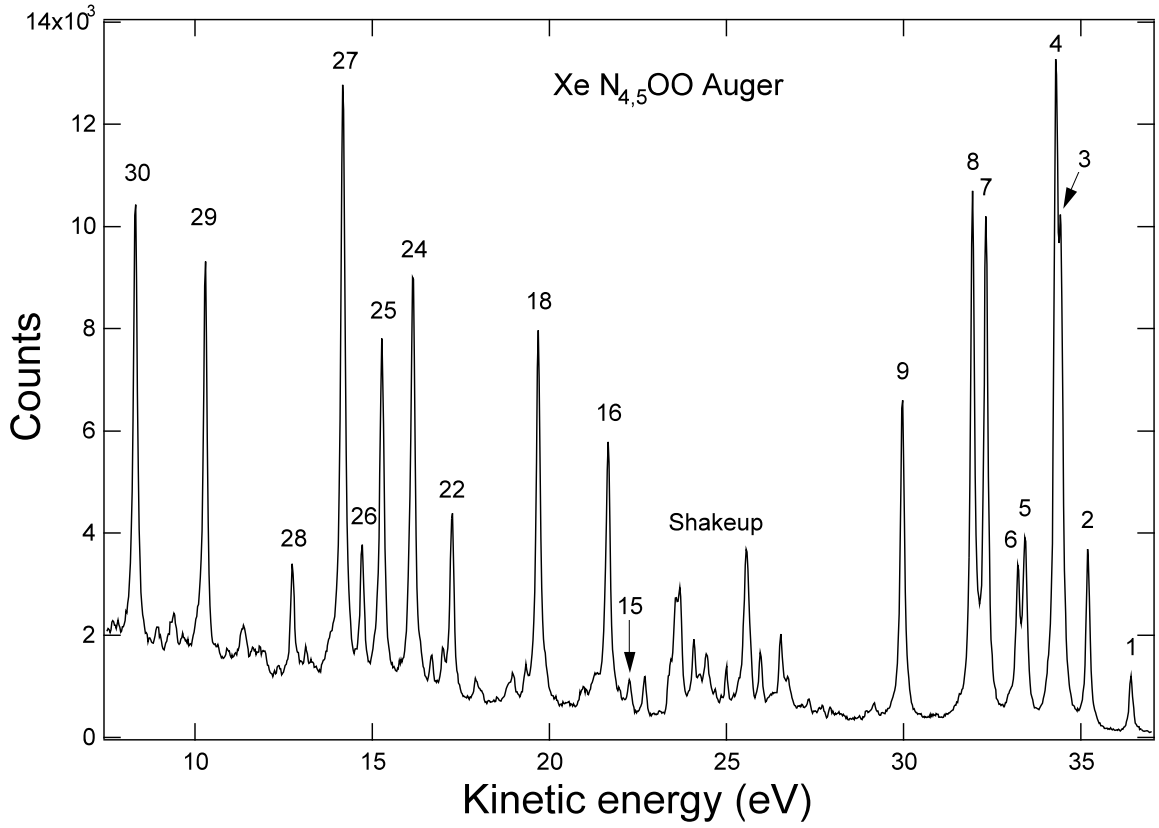
14x10^3
Xe N4,5OO Auger
Counts
Kinetic energy (eV)
0
2
4
6
8
10
12
10
15
20
25
30
35
30
29
28
27
26
25
24
22
18
16
15
Shakeup
9
8
7
6
5
4
3
2
1

Figure 1

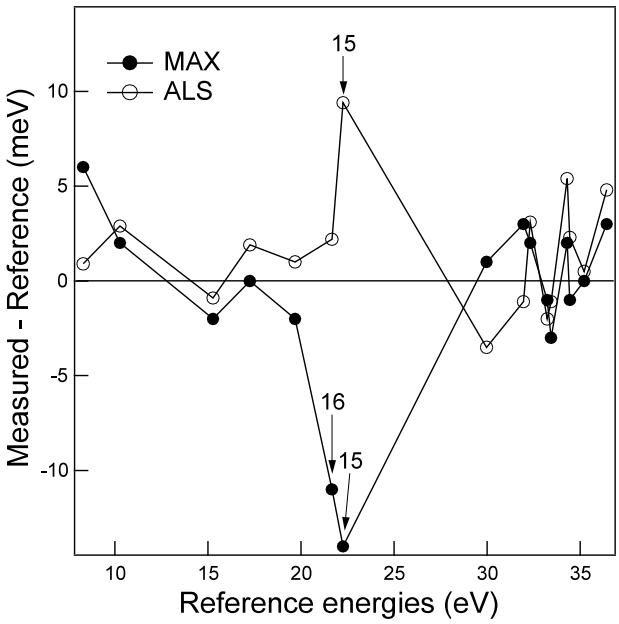
MAX
ALS
15
16
15
Measured - Reference (meV)
Reference energies (eV)
10
5
0
-5
-10
10
15
20
25
30
35

Figure 2

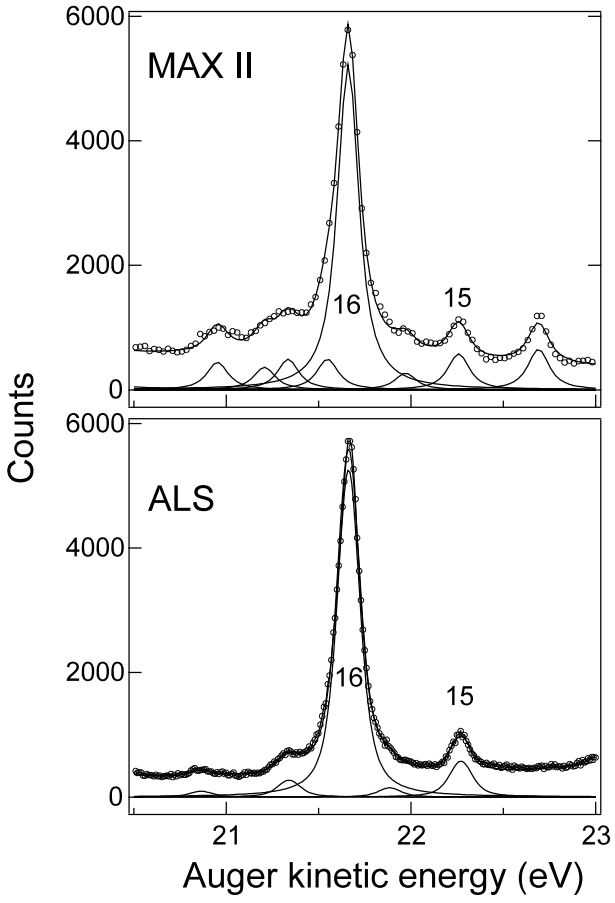
MAX II
ALS
16
15
16
15
6000
4000
2000
0
6000
4000
2000
0
Counts
21
22
23
Auger kinetic energy (eV)

Figure 3